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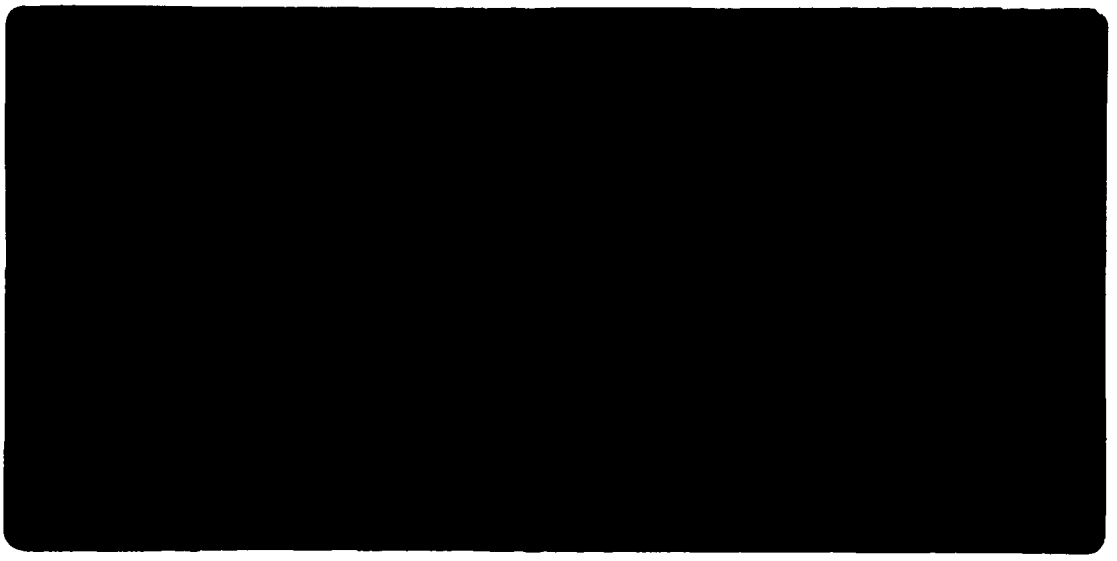

NUMBER 473

ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (VII): DEGRADATION REACTIONS OF β-METHOXY LIGNIN MODELS

D.R. DIMMEL, L.F. BOVEE, AND B.N. BROGDON

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ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (VII): DEGRADATION REACTIONS OF β-METHOXY LIGNIN MODELS

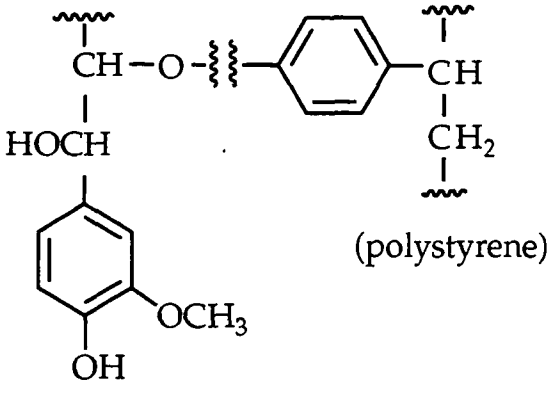
Donald R. Dimmel, Lois F. Bovee, and Brian N. Brogdon
The Institute of Paper Science and Technology
500 10th Street N.W., Atlanta, GA 30318

ABSTRACT

Two β-methoxy lignin model compounds were heated at 150°C in aqueous sodium hydroxide and in mixtures of NaOH/glucose and NaOH/glucose/AQ. Practically no β-ether cleavage was observed under these simulated pulping conditions. The principal products were vinyl ethers and C_α-reduction products; the former dominating in NaOH, the latter in the anthraquinone case. The observation of C_α-reduction products indicates that electron transfer reactions had occurred. Attempts to prepare β-(1-butenyl)-β-methoxy lignin models failed.

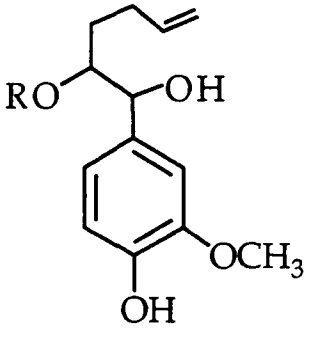
INTRODUCTION

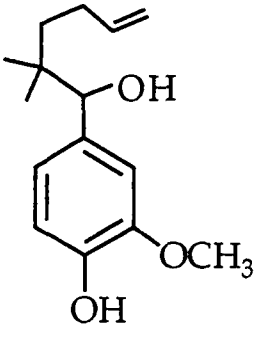
Lignin contains 50-60% β-aryl ether interunit linkages;[1] the cleavage of such linkages is quite important to the efficient removal of lignin during chemical pulping.[2] While β-alkyl ether linkages appear to be absent in native lignin samples, we became interested in the chemistry of β-methoxy lignin models for other reasons. If β-alkyl ether linkages were not broken under typical pulping conditions, we should be able to construct heterogeneous lignin model compounds of the type **1**, with the expectation that the lignin model portion would stay linked to the polymer under applied pulping conditions.[3]

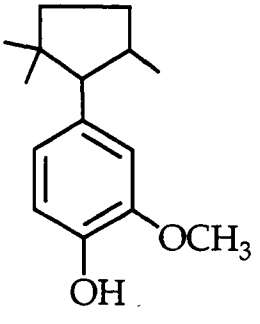


1

If β-methoxy cleavage was slow, models such as **2a** and **2b** could be used to study lignin electron transfer reactions. Such models more closely resembles lignin than does compound **3**, which in the presence of certain pulping reagents gives products, such as cyclic compound **4**, that indicate the occurrence of electron transfer reactions.[4,5] The rates of cyclization vs β-ether cleavage of the aryl and alkyl ethers **2a** and **2b** could be used to estimate the efficiency of electron transfer promoted lignin fragmentation reactions.







2a, R = Ar
2b, R = CH_3

3

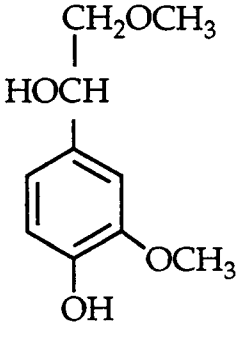
4

This paper describes the successful and unsuccessful synthesis of selected β-methoxy lignin models and reactions of two of the models.

RESULTS AND DISCUSSION

Synthesis

A simple β-methoxy lignin model **5** was prepared by reducing ketone **7** with $NaBH_4$; the ketone was prepared by reacting α-bromo-acetovanillone with $NaOCH_3$. Ketone **7** was alkylated with allyl bromide and 2-butenyl bromide to give ketones **8** and **9**. Reduction of **8** gave the β-allyl-β-methoxy alcohol **6**.



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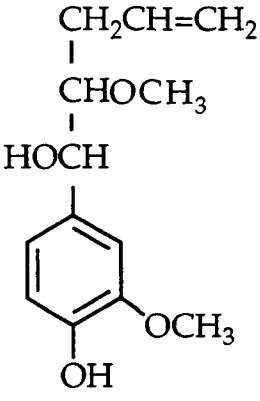

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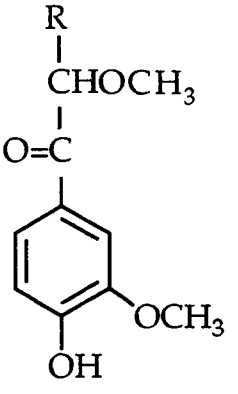
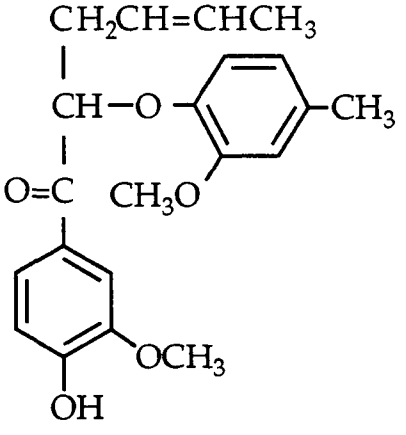
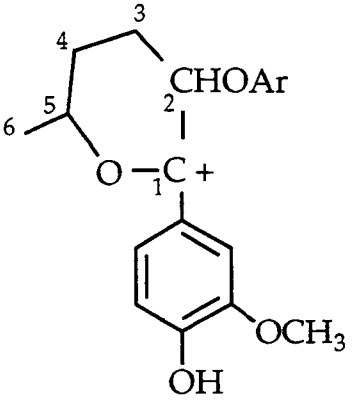


7, R = H
8, R = $CH_2CH{=}CH_2$
9, R = $CH_2CH{=}CHCH_3$
10, R = $CH_2CH_2CH{=}CH_2$



11



12

Numerous unsuccessful attempts were made to prepare the β-(1-butenyl)-β-methoxy ketone **10** by alkylation of **7** with 4-bromo and 4-iodo-1-butene. These results parallel trends observed for the alkylation of β-aryloxy ketones,[6] where alkylations were successful only in the cases of activated agents such as allyl and methyl halides. The β-(2-butenyl)-β-aryloxy ketone **11** was by alkylation of the corresponding β-aryloxy ketone with 2-butenyl bromide.

Various procedures were examined in an attempt to isomerize the double bonds in **9** and **11** to give β-(1-butenyl) compounds, such as **10**. Transposition of internal to external olefins is possible by hydroboration techniques;[7] however, seven attempts, with numerous variations, of this reaction failed to move the double bonds of **9** and **11**. Isomerization by hydrozirconation[8] also failed. Another strategy involved heating **11** with acid at different temperatures and with a 1:1 mixture of HCl and 2,6-lutidene. In the latter case, it was anticipated that (a) the double bond of **11** would be reversible protonated to give a mixture of C_4 and C_5 cations, (b) the C_5 cation would cyclize to give **12**, a relatively stable cation, and (c) a hindered base might react with **12** to deprotonate C_6 to give a β-(1-butenyl) compound. However, none of the acid catalyzed isomerizations were successful. Consequently, we were not able to prepare the desired target compounds **4a** and **4b**.

Kinetic Studies

Alcohols **5** and **6** were heated at 150°C in aqueous NaOH, both with and without additives, for different time periods. The choice of additives was based on comparing the best delignifying agent (AHQ) with the worst (NaOH alone) and to possibly show the existence of electron transfer reactions with the models. Glucose can both electron transfer[4] and promote delignification.[9] The product mixtures were analyzed for remaining starting materials (Figures 1 and 2) and liberated methanol. Duplicate data points were less reproducible for **5** than for **6**, where values were nearly identical (NaOH and NaOH/glucose at 60 min and NaOH/glucose/AQ at 30 and 60 min, Fig. 2).

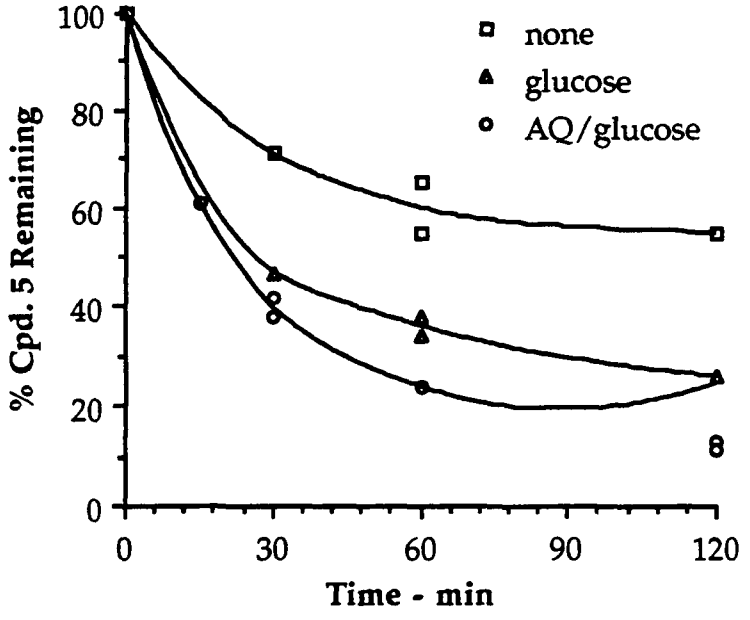


Figure 1. The Alkaline Degradation of 5 with Different Additives

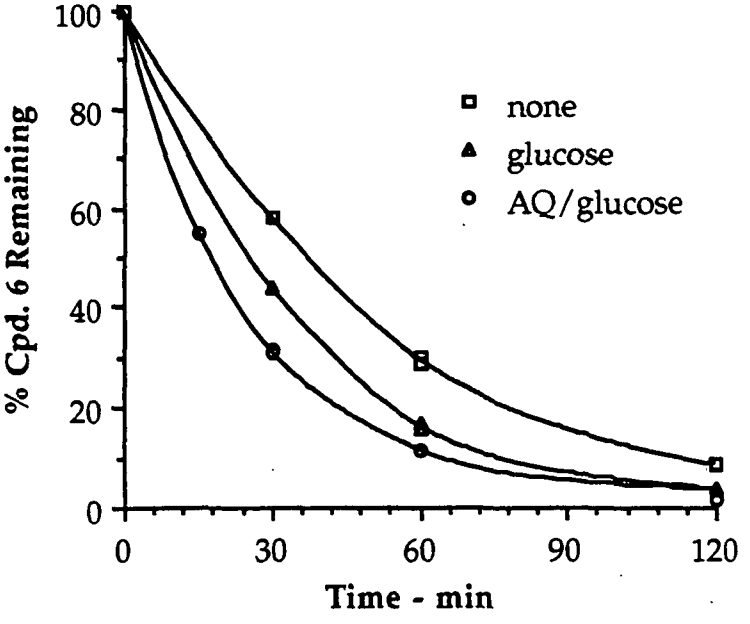


Figure 2. The Alkaline Degradation of 6 with Different Additives

For both alcohols, the disappearance of starting material with time followed the order: AHQ > glucose > NaOH. Alcohol **6** reacted faster than **5** under all conditions. Very little methanol (<1.5%) was liberated during the course of heating at 150°C under any of the conditions studied for either model. While methanol could have been released from the model by either β-methyl or aryl-methyl ether cleavage, the fact that its level of production did not increase with reaction time suggested that the observed methanol was an artifact.

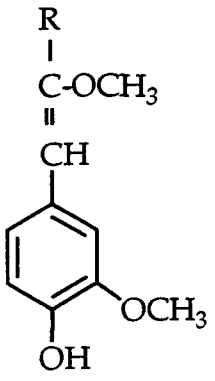
Product Studies

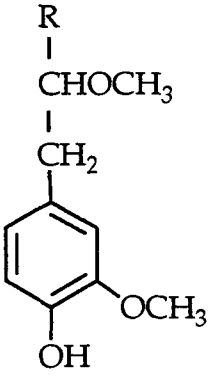
Product analysis for reactions of alcohol **5** presented problems with regard to vinyl ether content. Pure samples of **5** are difficult to prepare without some dehydration, resulting in vinyl ether contamination. In comparison to the β-substituted alcohol **6**, compound **5** was more prone to dehydration during storage, reaction, workup, and GC analysis. For these reasons, we focused our attention on the products of alcohol **6**. Based on the instability of **5**, the rate differences observed in Fig. 1 need to considered with caution.

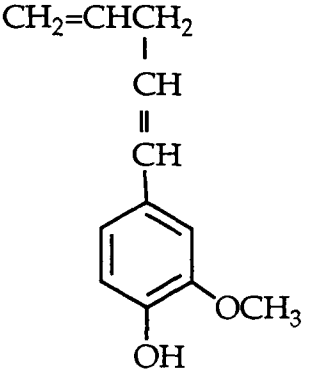
The products from alcohols **5** and **6** were primarily a result of dehydration (vinyl ethers **13** - **15**) and C_α-reduction (**16** - **18**). Except in the case of **17**, where isolation and full characterization was possible, most structural assignments were based on mass spectral data and NMR spectra of crude product mixtures. The vinyl ethers from the reaction of **6** with NaOH/glucose appeared to be largely cis/trans isomers (four possible) of the type **15**, rather than **14**. The assignment of product structures is discussed in depth in the Experimental Section.

The level of C_α-reduced products, **17** and **18**, was greatest for AHQ runs and least (not detected) in the NaOH runs. Compound **18** is probably derived from **17** by loss of methanol; the relative amounts of **17** and **18** may be an artifact of the product workup rather than actual formation differences during reaction.

In regard to reaction of **6**, a 2-hour AQ/glucose product mixture was composed of mostly reduction products **17** (major) and **18** (minor),







13, R = H
14, R = $CH_2CH{=}CH_2$
15, R = $CH{=}CHCH_3$

16, R = H
17, R = $CH_2CH{=}CH_2$

18

along with small amounts of residual starting material and vinyl ethers. A corresponding glucose run product mixture contained a similar product composition except that amounts of **17** and **18** were reversed and there was less **17** and **18** in comparison to starting material and vinyl ether products.

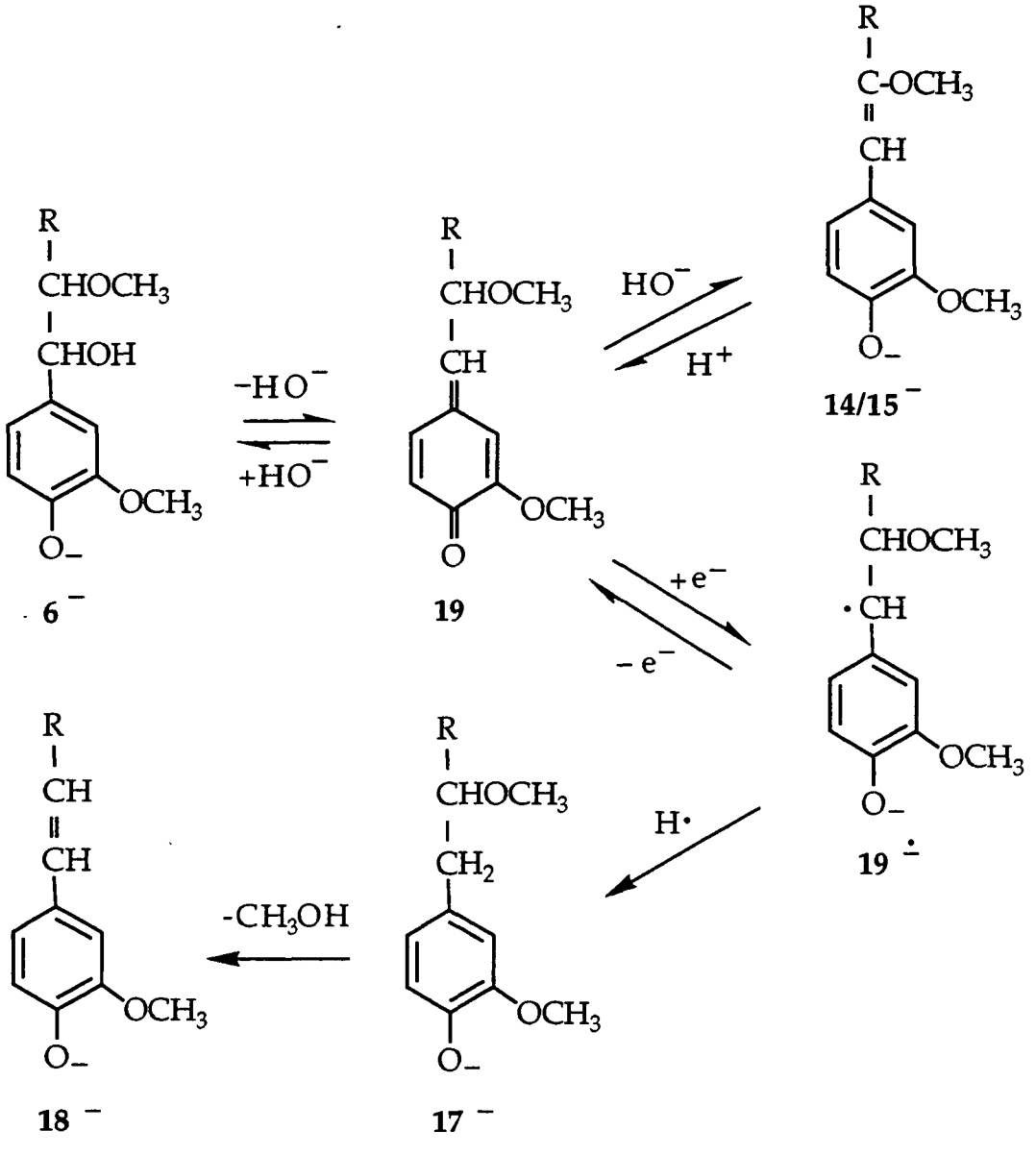
The same trends existed in the case of alcohol **5**, where the level of C_α-reduced product **16** was greatest for AHQ runs and not detected in the NaOH runs. The absolute amounts of **16** are more difficult to determine in this case because considerable amounts of vinyl ether products are formed with all additives.

Cyclization products, analogous to **4**, were not observed in the case of alcohol **6** under any of the conditions; their highest level should have occurred in NaOH/glucose runs.[4] Radical cyclizations appear to require a 5-hexenyl structural unit, rather than a 4-pentenyl unit,[10] which is what is present in alcohol **6**.

CONCLUSIONS

Degradation of the β-methoxy alcohol model **6** can best be understood by the set of reactions shown in Scheme 1. In alkali at high temperature, the alcohol is in equilibrium with a quinone methide intermediate (**19**).[11] Deprotonation of the C_β-H of the quinone methide

Scheme 1



gives vinyl ethers **14/15**. Electron transfer from AHQ^{-2} or glucose to **19** gives a radical anion intermediate **19˙⁻**, which can abstract a hydrogen atom from the additive to give a C_α-reduced product **17**. Such C_α-reductions have been observed in other systems which produce quinone methides in the presence of AHQ^{-2} or glucose.[4,12]

The differences in rates and relative product distributions for the different conditions employed can be explained by a rapid reduction of

the quinone methide intermediates by AHQ^{-2}, rather than a slower base-induced vinyl ether formation. In other words, AHQ^{-2} offers a second pathway for destruction and, thus, alcohols **5** and **6** are more rapidly depleted. Glucose alone can do the same, but is less efficient than AHQ^{-2}.

In all cases, direct cleavage of methyl ether-C_β bond is not observed; this is in sharp contrast to what happens with aryl ether-C_β bonds under similar conditions.[13]

EXPERIMENTAL

Melting points were determined on a Thomas Hoover capillary melting point apparatus. Infrared (IR) spectra, referenced against polystyrene, were obtained using sodium chloride discs on a Perkin-Elmer 700 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Jeol FX100 spectrometer at normal probe temperature. Electron impact mass spectroscopy (MS) employed a Hewlett-Packard 5985 instrument interfaced to a gas chromatograph, with helium carrier gas (30 mL min^{-1}), a source temperature of 200°C, an ionizing voltage of 70 eV, and a GC-MS interface of 250°C.

β-Methoxy-α-(4-hydroxy-3-methoxyphenyl)ethanol (5). The ketone **7** was reduced with 10 equiv. of $NaBH_4$ in 50% of EtOH, using a procedure previously described,[6] to give an oil; IR (neat) cm^{-1} 3400 (broad, OH) and 1600 (aryl); ^{1}H-NMR ($CDCl_3$) δ 2.9 (broad s, RO<u>H</u>), 3.43 (s, ROC<u>H</u>$_3$), 3.40 - 3.50 (m, 2, -C<u>H</u>$_2$-), 3.88 (s, 3, ArOC<u>H</u>$_3$), 4.82 (d of d, $J_{\alpha,\beta a}$ = 8 and $J_{\alpha,\beta b}$ = 4 Hz, 1, -C<u>H</u>$_\alpha$CH$_{\beta a}$H$_{\beta b}$-), 5.74 (s, 1, ArO<u>H</u>), and 6.83-6.93 (m, 3, Ar<u>H</u>); ^{13}C-NMR ($CDCl_3$) ppm 55.9 (q, ArO<u>C</u>H$_3$), 58.9 (q, RO<u>C</u>H$_3$), 72.4 (d, C_α), 78.2 (t, C_β), 108.7 (d, C_2), 114.2 (d, C_5), 119.0 (d, C_6), 132.1 (s, C_1), 145.1 and 146.4 (C_3 and C_4); MS *m/e* (%) 198 (M, 20), 153, (100), and 125 (19). The NMR spectra and GC analysis showed that the oil was >98% pure.

1-(4'-Hydroxy-3'-methoxyphenyl)-2-methoxy-4-penten-1-ol (6). The ketone **8** was reduced with 10 equiv. of $NaBH_4$ in 50% aq. EtOH

using a procedure previously described,[6] to give an oil which, based on analysis by GC and ^{1}H-NMR (C_α-C_β coupling constants[14]), was approximately a 55/45 mixture of erthro/threo isomers: IR (neat) cm^{-1} 3400 (broad, OH), 1640 (vinyl) and 1610 (aryl); ^{1}H-NMR ($CDCl_3$) δ 2.10 - 2.25 (m, 2, C$\underline{H}_2$), 2.3, 3.0 (s, 1, RO$\underline{H}$), 3.3 - 3.5 (m, 1, $C_2\underline{H}$), 3.39, 3.44 (s, 3, ROC$\underline{H}_3$), 3.89 (s, 3, ArOC$\underline{H}_3$), 4.47 (d, J = 7.3 Hz, 0.45, $C_1\underline{H}$-threo), 4.80 (d, J = 4.4 Hz), 0.55, $C_1\underline{H}$-erthro), 4.9 - 5.2 (m, 2, =C$\underline{H}_2$), 5.62, 5.64, (s, 1, ArO$\underline{H}$), 5.6-5.9 (m, 1, =C$\underline{H}$-), and 6.75 - 6.95 (m, 3, Ar-$\underline{H}$); ^{13}C-NMR ($CDCl_3$) ppm 33.5, 33.8 (t, C_3), 55.8 (q, ArO$\underline{C}H_3$), 58.0 (q, RO$\underline{C}H_3$), 73.5, 75.6 (d, C_1), 84.9 (d, C_2), 109.1, 109.3 (d, $C_{2'}$), 113.9, 114.0 (d, $C_{5'}$), 116.4, 117.2 (t, C_5), 119.1, 120.0 (d, $C_{6'}$), 132.2, 132.4 (s, $C_{1'}$), 133.6, 135.0 (d, C_4), 144.7, 145.1, and 146.2 (s, $C_{3'}$, $C_{4'}$); MS was the same for both stereoisomers, *m/e* (%) 238 (M^+, 7), 153 (100), 125 (11), 93 (27), 85 (14), and 65 (10).

β-Methoxy-4-hydroxy-3-methoxyacetophenone (7). A solution of 5 g of β-bromo-4-hydroxy-3-methoxyacetophenone[6] in 100 mL of dimethylformamide (DMF) was added dropwise to a stirred slurry of $NaOCH_3$ (10 equiv.) in 40 mL of DMF at 50°C under a nitrogen atmosphere. After complete addition and stirring for another 1 hour at 50°C, the solution was cooled, poured into 250 mL of ice water, acidified with 6 M HCl, and extracted three times with $CHCl_3$. The combined $CHCl_3$ extracts were washed with water, dried (Na_2SO_4) and evaporated. The resulting dark colored liquid (containing product and residual DMF) was purified by column chromatography, as previously described,[6] to give several fractions rich in product, which were recrystallized from toluene to give pure **7**: mp 73 - 74°C; IR (mull) cm^{-1} 3450 (OH), 1640 (C=O), and 1600 (aryl); ^{1}H-NMR ($CDCl_3$) δ 3.50 (s, 3, ROC$\underline{H}_3$), 3.94 (s, 3, ArOC$\underline{H}_3$), 4.67 (s, 2, -C$\underline{H}_2$), 6.3 (br s, 1, O$\underline{H}$), 6.94 (d of d, $J_{5\text{-}6}$ = 7.6 and $J_{5\text{-}2}$ = 1 Hz, 1, $\underline{H}_5$), 7.49 (d of d, $J_{6\text{-}5}$ = 7.6 and $J_{6\text{-}2}$ = 2 Hz, 1, $\underline{H}_6$), and 7.54 (slightly br s, 1, $\underline{H}_2$); ^{13}C-NMR ($CDCl_3$) ppm 55.8 (q, ArO$\underline{C}H_3$), 59.1 (q, ArO$\underline{C}H_3$), 74.6 (t, -$\underline{C}H_2$), 109.9 (d, C_5), 114.2 (d, C_2), 122.7 (d, C_6), 127.1 (s, C_1), 146.9, 151.0 (s, C_4, C_3), and 194.4 (s, C=O); MS *m/e* (%) 196 (M^+, 9), 166 (5), 151 (100), 123 (15), and 108 (7).

α-Allyl-α-methoxyacetovanillone (8). The alkylation procedure previously described[6] was applied on α-methoxyacetovanillone **(7)**

with 4 equivalents of lithium disopropylamine and 4 equivalents of allyl bromide. Purification of the product mixture by silica gel chromatography, elution with 0-10% EtOAc/CH_2Cl_2, gave an oil which displayed a single GC signal and spectral properties indicative of a pure substance, **8**: IR (neat) cm^{-1} 3350 (broad, OH), 1670 (C=O) and 1590 (br, aryl and vinyl); ^{1}H-NMR ($CDCl_3$) δ 2.57 (t, J = 6 Hz, 2, -CH-C$\underline{H}_2$-CH-), 3.37 (s, 3, ROC$\underline{H}_3$), 3.95 (s, 3, ArOC$\underline{H}_3$), 4.52 (t, J = 6 Hz, 1, C$\underline{H}_\beta$), 5.0-5.2 (m, 2, =C$\underline{H}_2$), 5.86 (d of d of t, J = 17.6, 9.6, and 6.8 Hz, 1, -CH-C$\underline{H}$=CH_2), 6.24 (s, 1, O$\underline{H}$), 6.95 (d, 1, J = 8.1 Hz, 1, $\underline{H}_5$), 7.61 (d, J = 2.0 Hz, 1, $\underline{H}_2$) and 7.71 (d of d, J = 8.3 and 2.0 Hz, 1, $\underline{H}_6$); ^{13}C-NMR ($CDCl_3$) ppm 37.6 (t, -$\underline{C}H_2$), 55.8 (q, ArO$\underline{C}H_3$), 57.4 (q, RO$\underline{C}H_3$), 83.6 (d, C_β), 110.6 (d, C_2), 114.0 (d, C_5), 117.4 (t, =CH_2), 123.7 (d, C_6), 127.4 (s, C_1), 133.1 (d, -$\underline{C}$H=), 146.7 (s, C_4), 150.9 (s, C_3), and 197.9 (C=O); MS *m/e* (%) 2366 (M^+, 4), 151 (100), 123 (8), 85 (27), 84 (8), and 55 (11).

1-(4'-Hydroxy-3'-methoxyphenyl)-2-methoxy-4-hexen-1-one (9). The procedure[6] used to prepare **8** was applied to convert ketone **7** to **9** by alkylating with 1-bromo-2-butene. Column chromatography[6] provided an oily product of >98% purity, consisting of two GC signals, in an 85/15 ratio, for the trans/cis isomers of **9**: ^{1}H-NMR ($CDCl_3$) δ 1.5-1.7 (m, 3, C$\underline{H}_3$-C=), 2.4-2.7 (m, 2, C$\underline{H}_2$-C=), 3.37 (s, 3, ROC$\underline{H}_3$), 3.95 (s, 3, ArOC$\underline{H}_3$), 4.47 (t, J = 6.3 Hz, 1, C$\underline{H}$OCH_3), 5.4-5.6 (m, 2, C$\underline{H}$ = C$\underline{H}$), 6.33 (s, 1, O$\underline{H}$), 6.95 (d, J = 8.3 Hz, Ar-$\underline{H}_{5'}$), 7.61 (d, J = 2.0 Hz, 1, Ar$\underline{H}_{2'}$) and 7.69 (d of d, $J_{6'-5'}$ = 8.3 and $J_{6'-2'}$ = 2.0 Hz, 1, Ar$\underline{H}_{6'}$); ^{13}C-NMR ($CDCl_3$) ppm 17.9 (q, $\underline{C}H_3$C), 36.6 (t, $\underline{C}H_2$C=), 56.0 (q, ArO$\underline{C}H_3$), 57.4 (q, RO$\underline{C}H_3$), 84.4 (d, $\underline{C}$HO), 110.6 (d, $C_{2'}$), 113.9 (d, $C_{5'}$), 123.8, 125.6, 126.5 (s, $C_{1'}$), 128.0 (d, $C_{6'}$, $\underline{C}$H=$\underline{C}$H), 146.6 (s, $C_{4'}$), 150.6 (s, $C_{3'}$), and 198.0 (s, C=O); MS was the same for both stereoisomers, *m/e* (%) 250 (M^+, 2), 218 (25), 167 (6), 151 (100), 123 (9), 99 (54), 98 (13), and 67 (23).

1-(4'-Hydroxy-3'-methoxyphenyl)-2-(2"-methoxy-4"-methylphenyl)-4-hexen-1-one (11). The procedure used to prepare **8** was applied to convert β-(2-methoxy-4-methylphenyl)acetovanillone[6] to **11** by alkylating with 1-1-broms-2-butene. Column chromatography[6] provided an oily product of >98% purity, consisting of two GC signals, 85/15 ratio, for the trans/cis isomers of **11**: ^{1}H-NMR ($CDCl_3$) δ 1.5-1.7

(m, 3, CH_3C=) 2.34 (s, 3, $ArCH_3$), 2.6-2.8 (m, 2, CH_2-C=), 3.76 (s, 3, $ArOCH_3$), 3.91 (s, 3, $ArOC\underline{H}_3$), 5.18 (t, J = 6.4 Hz, C<u>H</u>OAr), 5.5 - 5.6 (m, 2, C<u>H</u>=C<u>H</u>), 6.10 (s, 1, OH), 6.5 - 6.7 (m, 3, $Ar\underline{H}_{3'',5'',6''}$), 6.91 (d, J = 8.3 Hz, 1, $Ar\underline{H}_{5'}$), 7.67 (d, J = 2 Hz, 1, $Ar\underline{H}_{2'}$), and 7.69 (d of d, $J_{6'-5'}$ = 8.3 and $J_{6'-2'}$ = 2.0 Hz, 1, $Ar\underline{H}_{6'}$); ^{13}C-NMR ($CDCl_3$) ppm 12.9 (q, $Ar\underline{C}H_3$), 17.9 (=C$\underline{C}H_3$), 36.8 (t, $\underline{C}H_2$-C=), 55.8 (q, both $ArO\underline{C}H_3$), 82.7 (d, <u>C</u>H-O), 110.9, 113.5, 113.8, 116.5, 120.9, 124.0, 125.4, 128.3, 131.8 (Aryl and vinyl), 145.0, 146.4, 149.5, 150.5 (s, Ar-O) and 196.6 (s, C=O); MS was nearly the same for both stereoisomers, *m/e* (%) 356 (M^+, 22), 219 (38), 205 (17), 151 (100), 138 (49), 137 (52), and 123 (19).

Model Degradation Reactions. Degradations of **5** and **6** were carried out in 4-mL capacity, 316 stainless steel, pressure vessels (bombs).[15] The bombs were filled and sealed in a nitrogen atmosphere (glove bag); oxygen-free water was employed throughout. Sodium hydroxide solutions were prepared using oxygen-free water from a 30% ultrapure sodium hydroxide solution (Alfa Products). The model (0.375 mmoles) was dissolved 15 mL of 0.625M NaOH and 1 mL of this solution (0.025 mmoles of model) was placed in the bombs. For NaOH runs, 2.5 mL of water was added to the bombs to give a final volume of 3.5 mL and NaOH/model molar ratio of 25. For glucose runs, 1 mL of solution containing 562.5 mg of glucose in 25 mL of water (0.125 mmoles, 5 equiv.) was placed in the bombs, along with 0.4 mL of 0.625M NaOH and 1.1 mL of water; the additional base (35 equiv.) used in this case was because glucose degradation reactions consume NaOH. For anthraquinone experiments, 26 mg (5 equiv.) of AQ was weighed into each bomb before the liquids were added.

The bombs were tumbled in a preheated oil bath, removed after the desired reaction time, and immediately cooled in an ice-water bath. A base solution containing known amounts of two GC internal standards, *p*-isopropylphenol and ethanol, was added to the bombs. The bomb contents were removed and combined with two aqueous sodium hydroxide rinsings. The reaction sample was divided into two parts. The one part was acidified with hydrochloric acid until neutral and analyzed for methanol amount (relative to ethanol) by GC: 6 ft super Q

column, 100 - 150°C at 10°/min. The other part was reacted with a large excess of dimethyl sulfate and extracted with $CHCl_3$, which was then analyzed for methylated model amount (relative to methylated *p*-isopropylphenol) by GC: a 6 ft x 2 mm glass column containing OV-17 (3%) on Chromosorb W HP (100-120 mesh).

Degradation Products from Model 6. Two approaches were taken to examining the products. The first was to methylate (Me_2SO_4) the 2-hour kinetic run samples and analyze by GC-MS. The second was to combine the products from several bomb runs, separate the major components by column chromatography, and collect spectra data.

The 2-hour kinetic run sample for **6** in NaOH alone showed a single broad GC signal, which by MS analysis was a mixture of (methylated) starting material and vinyl ethers (**14/15**), with M^+ at 252 and 234. The 2-hour kinetic run sample for NaOH and glucose showed the same broad GC signal for the mixture of **6** and **14/15**, plus a minor signal for (methylated) **17** (M^+ at 236) and a major signal for (methylated) **18**: *m/e* (%) 204 (M^+, 100), 189 (70), 173 (65), 158 (55), 129 (55), and 115 (45). The 2-hour run sample for NaOH/glucose/AQ was similar to the glucose product mixture, except that **17** was the major component and **18** the minor one, and that the ratio of **6** + **14/15** to **17** + **18** was much smaller (more **6** had reacted).

Into 14 bombs were placed 40 mg of model **6**, 175 mg (5 equiv.) of AQ, 1 mL of 1M NaOH containing 5 equiv. of glucose, and 2.5 mL of 1M NaOH. The sealed bombs were tumbled in an oil bath at 135°C for 6 hr, cooled, opened, and the contents combined. The reaction mixture was acidified to pH 6 and extracted three times with $CHCl_3$. The combined $CHCl_3$ extracts were dried (Na_2SO_4), filtered, and evaporated. The resulting oil was analyzed by GC/MS and separated by column chromatography; 180 fractions were collected. Fractions 80-109, which contained >96% pure **17** (by GC and TLC), were combined, concentrated, and an NMR recorded (proton decoupling was employed to aid in the assignments): ^{1}H-NMR ($CDCl_3$) δ 2.31 (rough triplet, J = 6-7 Hz, 2, C_3 $C\underline{H}_2$), 2.69 and 2.71 (d, J = 6 Hz in each case, 2, C_1 nonequivalent $C\underline{H}_2$), 3.40 (p, J = 6 Hz, 1, CH_2-$C\underline{H}$-CH_2), 3.86 (s, 3, $OC\underline{H}_3$), 4.9-5.3 (m, 2, =$C\underline{H}_2$),

5.55 (s, 1, O<u>H</u>), 5.6-6.1 (d of d of t, J = 7, 11, and 12 Hz, 1, -C<u>H</u>=), 6.67 (d of d, J = 2.0 and 7.5 Hz, 1, $C_{5'}$<u>H</u>), 6.72 (br s, 1, $C_{2'}$<u>H</u>), and 6.83 (d of d, J = 1.2 and 7.5 Hz, 1, $C_{6'}$<u>H</u>); ^{13}C-NMR ($CDCl_3$) ppm 37.6 and 39.6 (t, <u>C</u>H_2-CH-<u>C</u>H_2), 55.8 (q, ArO<u>C</u>H_3), 56.9 (q, RO<u>C</u>H_3), 81.8 (d, CH_2-<u>C</u>H-CH_2) 112.0 (d, $C_{2'}$), 114.0 (d, $C_{5'}$), 116.7 (t, =<u>C</u>H_2), 121.8 (d, $C_{6'}$), 130.5 (s, $C_{1'}$), 134.5 (d, -<u>C</u>H=), 143.8 (s, $C_{4'}$), 146.1 (s, $C_{3'}$); MS *m/e* (%) 222 (M^+, 40), 181 (43), 138 (28), 137 (58), 85 (100), and 55 (21). A GC/MS analysis of a NaOH-glucose-AQ degradation of **6** done at 150°C for 2 hr also showed that **17** was the major component of the product mixture.

A similar 14 bomb reaction was performed at 150°C for 5 hr with model **6**, only no AQ was present. Each bomb contained 100 mg of glucose and 150 mg of amylose, along with the 1M NaOH. [The amylose degrades more slowly than glucose in NaOH solution and thereby provides a long lasting "glucose."] None of the column chromatography fractions contained single components. Fractions 165-180, which contained the bulk of the products, were combined, concentrated, and spectra recorded. A GC-MS of the product mixture showed: main products **17** and **18**, *m/e* (%) 190 (M^+, 100), 175 (72), and 115 (50); minor products guaiacol and an unknown, *m/e* (%) 204 (M^+, 100), 189 (40), and 161 (50); very minor products **14** and **15**, *m/e* (%) 220 (M^+, 100), 205 (40), 173 (60), and 145 (45). [The crude product before chromatography showed more vinyl ether components (**14/15**) than did the isolated chromatography fraction; still **14/15** were not major products.] The ^{1}H-NMR spectrum for combined fractions 165-180 showed the presence of **17** and substantial signals in the δ 1.2-1.9 region (C<u>H</u>$_3$C= and C<u>H</u>$_2$C=), 3.87-3.91 (ArOC<u>H</u>$_3$ and =COC<u>H</u>$_3$),[11] 5.6-6.6 (=C<u>H</u>), and 6.8-6.9 (electron-rich Ar<u>H</u>); except for **17**, there were no other signals associated with aliphatic methoxyl groups and terminal olefins (=CH_2). The ^{13}C-NMR also showed **17**, together with an abundant ArO<u>C</u>H_3 and =CO<u>C</u>H_3) signal,[11] strong aryl/vinyl signals, and only a few weak aliphatic signals (i.e., 29.7). The NMR spectral evidence agrees with the structural assignments proposed by GC-MS.

Degradation Products from Model 5. A single bomb run at 150°C for 1 hr with 6.1 mg of **5**, 31.2 (5 equiv.) of AQ, 27.1 (5 equiv.) of glucose,

and 3.5 mL of 0.3M NaOH was performed. After cooling, the bomb contents were worked up as above and analyzed by GC/MS. Only three components were present: AQ, cis/trans vinyl ethers **13**, and C_α-reduced model **16**. A similar run with glucose, but with no AQ present, showed (by GC-MS): starting material, cis/trans vinyl ethers **13**, and trace levels **16**. The mass spectra were as follows: cis/trans vinyl ethers **13**, *m/e* (%) 180 (80, M^+), 137 (22-37), and 133 (100); **16**, *m/e* (%) 182 (4, M^+) and 137 (100, C_α-C_β cleavage).

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